Society. Thanks are also given to Mr. Anthony D'Addario for his help in the structural analysis.

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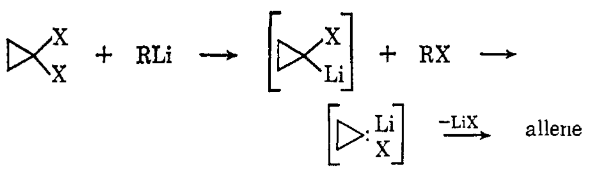
## An Investigation of the Reaction between 1,1-Dichlorocyclopropanes and Alkyllithium Reagents Using Chemically Induced Dynamic Nuclear Polarization

*Sir:*

The reactions of *gem*-dihalocyclopropanes with alkyllithium compounds have been applied to the synthesis of allenes[1] and of strained polycyclic systems.[2] The reaction sequence, in the case of allene formation, is generally accepted to proceed first to an $\alpha$-halolithium intermediate, then, perhaps, through a carbene–lithium halide complex. The intermediacy of $\alpha$-halolithium compounds has been established in other *gem*-dihalide systems by trapping at low temperatures,[3] but no direct evidence is available in the *gem*-dihalocyclopropane series.



Since the formation of the $\alpha$-halolithium intermediates involves a halogen–metal exchange, it seemed appropriate to search for chemically induced dynamic nuclear polarization (CIDNP), which has been found in other halogen–metal exchange reactions.[4] The CIDNP phenomenon depends on the polarization of nuclei (protons in this case) in short-lived free-radical intermediates and is observed by scanning the nmr spectrum of the reacting solution.[5] Both enhanced absorption (+ polarization) and emission (− polarization) arise from the protons of the products of free-radical reactions.

We have examined the reaction of 1,1-dichloro-2,2-dimethylcyclopropane (**1**) with ethyllithium in benzene–ether (30:1) at *ca.* 40° to give 3-methyl-1,2-butadiene (**2**) and 1-chloro-2,2-dimethylcyclopropane (**3**) as major products. Figure 1 shows the nmr spectrum[6] taken (a) before the reaction was initiated by the addition of ether,[7] (b) during the reaction, and (c) at its completion.

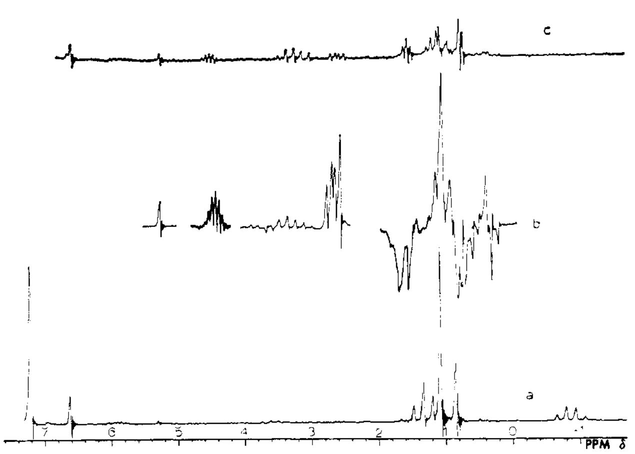


Figure 1. (a) Nmr spectrum of a solution of ethyllithium and **1** in benzene; (b) composite of several scans taken within seconds after ether has been added to initiate the reaction; (c) scan after the reaction is complete; benzene amplitude is × 0.1.

Because the maximum polarization often can be observed only for a short time compared to the time needed for a complete scan, Figure 1b is a composite of scans of different regions of the spectrum taken at the appropriate time in several reactions run under similar conditions. The effect of polarization on the protons of both of the major reaction products is observed. For the allene **2**, the vinyl protons ($\delta$ 4.45) show + polarization; the methyl protons of **2** may be polarized but do not account for all of the emission observed at $\delta$ 1.4–1.9. The proton $\alpha$ to the chlorine in **3** is strongly polarized (doublet of doublets at $\delta$ 2.61), and the emission and enhanced absorption at $\delta$ 0.25–0.6 match very well with an authentic absorption spectrum of **3**, although additional lines are present.

The use of emission as proof for polarization is not open to question, but lines which show only enhanced absorption must be more critically examined to exclude the possibility that the change in absorption intensity results from a rapid product formation and subsequent destruction by further reaction. If the polarization is sufficiently intense, however, its presence can be established conclusively by a comparison of the absorption intensity with the maximum intensity possible if all of the starting material were converted to the product in question. For example, the observed area of the septuplet at $\delta$ 4.45 (two protons) is twice as large as the singlet for the methylene protons in the starting material **1** (also two protons). The absorption in the same region at the end of the reaction is proper for the 44% yield of **2** as analyzed by gas chromatography.

We believe that these results are best explained by the sequence in Scheme I. Transfer of an electron from ethyllithium to **1** gives a caged radical pair which can disproportionate to give **3**, couple to give **4**, or transfer an electron either to return to **1** or proceed to the $\alpha$-halolithium intermediate **5**. Proton polarization occurs in the free radicals before reaction to give diamagnetic products. Evidence for the return to **1** rests on the emission line at $\delta$ 0.85, but the identity of this line is still open to question.

The polarization at $\delta$ 2.61 is unique, comprising the first example of a nucleus which is polarized in one free

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(1) W. R. Moore and H. R. Ward, *J. Org. Chem.*, 27, 4179 (1962); L. Skattebøl, *Tetrahedron Letters*, 167 (1961).

(2) W. R. Moore, H. R. Ward, and R. F. Merritt, *J. Am. Chem. Soc.*, **83**, 2019 (1961).

(3) D. F. Hoeg, D. I. Lusk, and A. L. Crumbliss, *ibid.*, **87**, 4147 (1965).

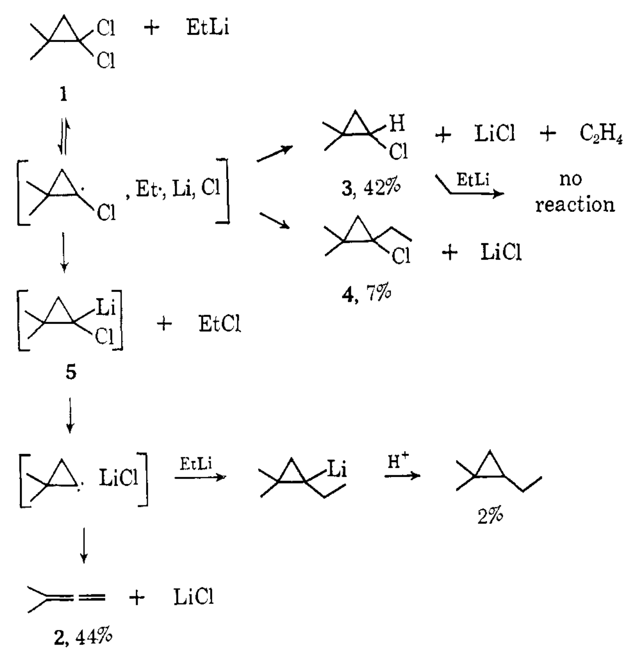
(4) H. R. Ward, R. G. Lawler, and R. A. Cooper, submitted for publication.

(5) H. R. Ward and R. G. Lawler, *J. Am. Chem. Soc.*, **89**, 5518 (1967).

(6) Spectra were taken on a Varian A-60-A at 1000-Hz sweep width. The spectrometer was purchased with funds supplied by the National Science Foundation.

(7) J. K. Eastham and G. W. Gibson, *J. Am. Chem. Soc.*, **85**, 2171, (1963).

**Scheme I**



radical, is transferred during a radical disproportionation, and exhibits enhanced absorption in the new molecule. Specifically, the $\alpha$-halo proton in **3** probably was polarized in the ethyl radical before hydrogen atom transfer occurred.

If the idea of the intermediacy of **5** is valid, then, since polarization continues into the allene, there is a possibility of direct observation of CIDNP from **5**. Some of the unassigned emission and enhanced absorption between $\delta$ 0.17 and 0.83 may be tentatively assigned to **5**, but we have not yet been able to prepare **5** at low temperatures for a comparison absorption spectrum. The fact that CIDNP is observed in **2** places the proton relaxation time (a few seconds) as an upper limit on the lifetime of **5** under the reaction conditions.[8]

When *n*-butyllithium or *t*-butyllithium reacts with **1**, polarization can be observed from the protons in the olefin formed by disproportionation.[9] This polarization is of a single sign for a particular proton at a particular time (*e.g.*, the vinyl protons of isobutylene show only emission), distinctly different from the isobutylene formed in the reaction of *t*-butyllithium and *n*-butyl bromide[5] where the vinyl protons exhibit both positive and negative polarization effects.

The observation of CIDNP phenomena seems to offer continued promise as a technique for the investigation of unstable intermediates which result from one-electron transfers.

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(8) The polarization of nuclei in 2 may also arise from the intermediacy of a triplet-state carbenoid species in the reaction of 5. Such a double "paramagnetic pulse" seen by the nuclei on the route from 1 to 2 may be difficult to establish in the absence of isolation of 5 as a stable species. Nuclear polarization also may arise from the intermolecular dipolar interaction generated during nonreactive encounters between free radicals and proton-containing molecules in solution (K. H. Hausser and D. Stehlik, *Advan. Magnetic Resonance*, 3, 79 (1968). However, strong positive polarization of solvent protons has not been observed (to our knowledge) in dynamic nuclear polarization experiments on electromagnetically pumped solutions of neutral free radicals. The positive polarization seen in the present example requires an unprecedented time-dependent scalar coupling between the unpaired electron of a neutral free radical and the protons of surrounding molecules, if it is to occur by intermolecular interaction.

(9) The absorption of the ethylene in Figure 1b is more intense than in the product (Figure 1c), but some of the diminution of signal may be from the escape of ethylene from solution; polarization has not been established in this case.

(10) National Center for Air Pollution Control Special Fellow (predoctoral).

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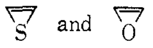
## The Mechanism of the Wolff Rearrangement

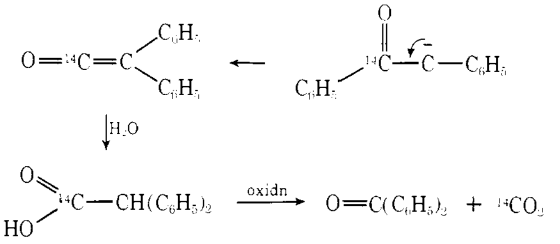
*Sir:*

MO calculations recently performed by us on the three-membered strained ring systems



predict a singlet ground state with low stability for both species. A similar result was reported earlier for the sulfur compound by Zahradnik.[1] We could experimentally verify this prediction for thiirene by observing the transient existence (with half-lives of up to several seconds) of thiirene and its homologs in the gas-phase addition reactions of sulfur atoms to acetylenes and in the photolysis of 1,2,3-thiadiazole.[2]

Oxiirene, however, has not yet been detected. It has been postulated as an intermediate in the peroxyacid oxidations of acetylenes[3] and considered in the decompositions of $\alpha$-diazo ketones. Franzen[4] has attempted to elucidate the mechanism of the Wolff rearrangement, the isomerization of $\alpha$-keto carbenes to the ketene structure, by using $^{14}$C-labeling techniques. Photolysis and thermolysis of [$^{14}$C]azibenzil were carried out in dioxane–water–triethylamine and dioxane–water solutions, and the position of the $^{14}$C atom in the resulting diphenylacetic acid was determined by oxidative decarboxylation followed by measurement of the radioactivity of the carbon dioxide. It was concluded that oxiirene is not an intermediate and the reaction proceeds *via*



since all radioactivity appeared in the carbon dioxide product. This result agreed with that of a similar study reported earlier by Huggett, *et al.*[5] Thus for these reasons it has since been generally accepted that the Wolff rearrangement does not involve the oxiirene intermediate.[6]

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(1) R. Zahradnik, *Advan. Heterocyclic Chem.*, 5, 14 (1965).

(2) O. P. Strausz, J. Font, E. L. Dedio, P. Kebarle, and H. E. Gunning, *J. Am. Chem. Soc.*, 89, 4805 (1967).

(3) J. K. Stille and D. D. Whitehurst, *ibid.*, 86, 4871 (1964); R. N. McDonald and P. A. Schwab, *ibid.*, 86, 4866 (1964).

(4) V. Franzen, *Ann.*, 614, 31 (1958).

(5) C. Huggett, R. T. Arnold, and T. I. Taylor, *J. Am. Chem. Soc.*, 64, 3043 (1942).

(6) E. S. Gould, "Mechanism and Structure in Organic Chemistry," Holt, Rinehart and Winston, New York, N. Y., 1960; W. Kirmse, "Carbene Chemistry," Academic Press, New York, N. Y., 1964.